

**PCT**WORLD INTELLECTUAL PROPERTY  
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER 1

WO 9607538A1

<p>(51) International Patent Classification 6 : B32B 5/16, 9/00, 15/02, 17/02, 17/04, 27/02, 27/04, B01J 13/02, 13/04, 13/20, 13/22, C23C 14/00, 14/58, 20/02, 20/04, C03B 19/10, 19/12, 19/14, 37/00, C03C 17/06, 17/34, 17/36, 25/02, 25/04</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 96/07538</b>  (43) International Publication Date: 14 March 1996 (14.03.96)</p>
<p>(21) International Application Number: PCT/US95/11340 (22) International Filing Date: 6 September 1995 (06.09.95) (30) Priority Data: 08/300,961 6 September 1994 (06.09.94) US (71) Applicant: THERMACELL TECHNOLOGIES, INC. [US/US]; 212 Lake Harris Drive, Lakeland, FL 33813 (US). (72) Inventors: MARTIN, Alfred, J.; 7290 Fosdick, Saline, MI 48176 (US). PIDORENKO, John; 925 Beaver Crossing Lane, Saline, MI 48176 (US). (74) Agents: OBERHOLTZER, Steven, L. et al.; Harness, Dickey &amp; Pierce, plc, P.O. Box 828, Bloomfield Hills, MI 48303 (US).</p>		<p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  Published With international search report.</p>
<p>(54) Title: INSULATION MICROSPHERES AND METHOD OF MANUFACTURE</p>		
<p>(57) Abstract</p> <p>Evacuated microspheres (10) and insulating materials constructed from such microspheres (32) provide insulation and reduce heat transfer through radiation, conduction and convection. Additionally, an infrared reflective coating (16) is provided on a microsphere surface to reduce radiant heat transfer. A protective exterior coating (18) is also provided to protect an exteriorly applied infrared reflective coating on such a microsphere. The evacuated microspheres are used in elastomeric roof coatings or exterior paints.</p> <div data-bbox="873 1150 1258 1690"><p>10 12 14 16 18</p></div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## INSULATION MICROSPHERES AND METHOD OF MANUFACTURE

**FIELD OF THE INVENTION**

This invention relates to thermal insulating materials and more particularly to evacuated glass or polymeric microspheres and insulating coatings incorporating such microspheres, as well as methods of manufacturing same.

**BACKGROUND OF THE INVENTION**

Hollow microspheres and methods of producing them are presently known. Typically, these microspheres are utilized to form insulation materials and coatings. In one method of construction, a blowing glass is used to form hollow microspheres. Small glass particles are introduced into a heated zone, for example a furnace, where the elevated particle temperature decreases the glass' viscosity such that the glass behaves as a liquid and readily flows. The glass particles which have low viscosity and surface tension form glass droplets. Microscopically small bubbles form inside the droplets by a gas dissolved in the glass feed particles or generated from the volatilization of blowing agents which have been incorporated in the glass feed particles. The small bubbles coalesce to form a single and larger void within the glass droplet thereby producing a glass "bubble". The glass bubble expands in response to the blowing gases produced within the feed particles, in addition to the in-permeation of ambient gases while the bubble is held in the heated zone. Expansion stops when the bubble's internal pressure balances with forces produced by the combination of surface tension on the glass and the external ambient pressure. When bubbles exit the heated zone and are exposed to much lower temperatures, they rapidly solidify due to their relatively small heat capacity, thereby forming solid glass shells. Typically, this technique produces shells having a diameter ranging from approximately 5 microns to approximately 5,000 microns. However, all commercial shell manufacturing processes carried out in this general manner produce shells which contain appreciable residual gases.

The performance of thermal insulation is routinely described in terms of an R-value and an R-value/inch. The R-value/inch is the same as the reciprocal effective thermal conductivity, in the units of  $\text{hr-ft}^2\text{-}^\circ\text{F}/\text{BTU-inch}$ . As an example, conventional fiberglass insulation has an R-value/inch of 3 or more, and an R-value for a 9 and 1/2 inch layer is 30, all numbers for normal room temperature. However, an inch of stagnant air has a higher R-value, 5.5. The fiberglass is needed to preclude convection, bulk movement of air, which if allowed to occur significantly decreases the R-value, much more so than does the presence of the fiberglass, which is an alternative conduction path. Much higher performance insulation materials and configurations are needed. Hollow microspheres are an alternative insulation material with improved thermal performance characteristics.

The use of evacuated glass microspheres as an important component of improved insulation has been recognized for some time. The use of a reflective layer within or outside of such a shell has also been referred to. An excellent reference to these effects is the patent by Torobin, U.S. Patent No. 4,303,732. Torobin reports R-value/inch of 3 to 11 for glass shells with a low thermal conductivity gas within the shell; an R-value/inch of 5 to 15 for glass shells with a low thermal conductivity gas within the shells and a low emissivity, reflective coating; an R-value/inch of 25 to 35 for evacuated shells with a low emissivity reflective layer; and other ranges of R-value/inch, up to 70, for alternative insulation configurations. The specific details of the microspheres, such as sphere aspects ratio are not reported.

To produce better-value insulation based upon the incorporation of shells in the overall insulation, efforts have focused upon shell evacuation to minimize the thermal conduction of the contained gas and on producing a high aspect ratio shell to minimize the shell-wall conduction, but with limited success. As a review, the effective thermal conductivity of shells is a function of the shell aspect ratio, wall material (such as glass or polymer) and the shell gas composition and pressure. In general, the lower the thermal conductivities of the wall material and the internal gas, the lower the effective shell thermal conductivity. For the internal gas the higher the effective molecular weight, nominally, the lower the thermal conductivity. For example, at 120°F the thermal conductivities of hydrogen, steam, air, CO<sub>2</sub>, SO<sub>2</sub> and butane (gas) are 0.115, 0.014(5), 0.016, 0.01, 0.0060 and 0.011 BTU-ft/hr-°F-ft<sup>2</sup> ("Chemical Engineering Handbook", 3rd Edition, Perry, McGraw-Hill). At sufficiently low pressures the mean free path of the gas molecules is large compared to the shell inner diameter and the conduction through the gas becomes much less, and essentially linear with pressure. For a particular gas in shells of approximately 100 micron inside diameter, the thermal conductivity decreases as the gas pressure decreases below a few Torr. Under these conditions the lower the pressure the lower the thermal conduction through the internal gas. However, there are practical limits to how low a gas pressure is needed depending upon the shell wall material and shell aspect ratio. For each case there are diminishing return limitations.

Under some conditions the conduction through the shell wall can dominate (as for example a low aspect ratio shell of a high thermal conductivity wall material) the overall heat transfer, regardless of the internal gas pressure and composition. Both glass shells and polymer shells are available. The thermal conductivity of the polymers (approximately 0.1 BTU-ft/hr-°F-ft<sup>2</sup>) used for shells is much lower than that for glasses (approximately 0.6 BTU-ft/hr-°F-ft<sup>2</sup>) used for shells. Thus polymer shells are preferred for selected applications for which their other properties are acceptable. Glass shells are, however, the dominant candidates for insulation applications. The shell aspect ratio must be as high as feasible to minimize the shell thermal conductivity. The manufacturing process and application conditions dictate the aspect ratio. However, there are limits to how high the shell aspect ratio can realistically be for the particular application. Mechanical loading on the shells, for example, can cause loss of mechanical integrity and thus pose a limit on aspect ratio.

To maximize the possible insulation value of micro shells, attempts have been made to evacuate shells or directly manufacture evacuated shells. One apparently successful out-permeation of residual gases from borosilicate glass shells (type B12AX produced by the 3M Corporation) was reported by Parmley and Cunnington, (R.T. Parmley and G.R. Cunnington, "An Ultra-lightweight, Evacuated, Load-bearing, High Performance Insulation System," Proceedings of 2d AIAA and ASME Thermophysics and Heat Transfer Conf., Palo Alto, CA, (1978)). Residual gases in such shells were reported to be 99.97% SO<sub>2</sub> and 0.03% air, at a total pressure of  $2.1 \times 10^{-2}$  Torr. Parmley and Cunnington claim to have obtained internal pressures of  $\leq 0.1$  mTorr by baking shells in a vacuum at nominally 421°C for 20 days. The aforementioned glass shells (type B12AX) were an experimental product being developed by 3M. Currently, shells of essentially the same glass composition (a soda-lime borosilicate) and containing similar gases are commercially available from 3M.

As an example of attempts to manufacture evacuated shells refer to Torobin, U.S. Patent 4,303,732, which reveals a process for manufacturing vacuum microspheres. This process is based on blowing individual

shells from a molten glass using a coaxial nozzle. The blowing gas flows through the inner nozzle and the glass flows through the annulus about the inner nozzle thereby forming a glass bubble, which is subsequently detached by vibration or the action of a second transverse gas stream.

The vacuum can be formed by any of several ways, such as entraining into the blowing gas, particles  
5 of metal or metal organic compounds which will become gaseous at the molten glass temperature, and which upon cooling will re-solidify and form a reflective film on the inner surface of the microshell. The residual gas pressure at room temperature results from any trace in-permeated gas plus the vapor pressure of the metal. With a proper choice of metals, the film will exhibit a very low vapor pressure. Apparently, this process has been successfully demonstrated, but is not commercially viable.

10 Cox, in U.S. Patent No. 3,607,169, reveals a similar process. Again, the production of the shell is based on the use of metals as blowing agents. In this case, glass-coated metal particles are made by an extrusion method. As in the case of the Torobin patent, this process is not commercially practiced.

Sowman, in U.S. Patent No. 4,349,456, reveals a process for making ceramic metal oxide shells, which is nevertheless similar to Cox and Torobin in that it also requires generating individual feed particles  
15 or droplets. The process does not utilize a blowing gas. It consists of forming droplets of an aqueous metal oxide sol and introducing them into a dehydrating liquid which rapidly removes the water from the droplet forming a gelled microcapsule. These microcapsules are then recovered by filtration, dried, and fired to convert them into shells. Prior to firing, the microcapsules are sufficiently porous that when placed in a vacuum during the firing process the gases can be removed, and subsequently the resulting shells will  
20 generally be impermeable to ambient gases. This process is not commercially practiced.

As examples of a different approach to microshell manufacture, one that employs steam as a furnace atmosphere component, refer to Manabe et al., in U.S. Patent No. 4,693,739 and Downs and Miller, in U.S. Patent No. 4,336,338. In these references significant partial pressures of steam as furnace atmospheres are used to obtain advantages in the production of microspheres. There is also reference to water dissolved in  
25 the shell material to act as a blowing agent. These two patents do not claim to give evacuated microshells, but do represent an alternative manufacturing scheme that has useful characteristics that we plan to expand upon and further develop to produce microshells that have much more easily removed enclosed gas.

#### SUMMARY OF THE INVENTION

30 Pursuant to this invention, microspheres, insulating coatings containing same, and a method of constructing same, are provided with shells formed from glass or polymeric material which is substantially evacuated to impart a high thermal insulation value. Coatings containing such insulating microspheres will likewise have a high insulating value.

When forming insulating layers, it is desirable to reduce the heat transfer which occurs between  
35 surfaces at different temperatures by all three heat transfer mechanisms, namely radiation, conduction (through both solids and gases) and convection, when possible and appropriate. The microspheres of this invention can provide characteristics which reduce all three heat transfer mechanisms. The insulation applications of this invention use material shells of such small characteristic dimensions such that convection effects are unimportant. Conductive heat transfer and radiative heat transfer are functions of material  
40 selections and design and performance requirement considerations, and are to be minimized.

To reduce conductive heat transfer, two general aspects of microshell design and manufacture are important. The first is related to the shell wall, the aspect ratio and the wall material; the second is related to the contained gas, the composition and pressure. In terms of shell wall, the lower the thermal conductivity of the wall material and the higher the aspect ratio of the shell, the lower the conductive heat transfer. As an example, polymeric wall material has an appreciably lower thermal conductivity than glass. Thus, the use of such low thermal conductivity polymer is preferred where this is consistent with other application considerations. Similarly, as high a shell aspect ratio as feasible, consistent with other application considerations, is preferred. In these manners the thermal conduction contribution by the shell wall can be minimized.

10 In like consideration, the thermal conduction contribution of the microshell gas content can be lessened by the appropriate choice of internal gas composition and total pressure. A lower thermal conduction contribution is associated with a higher molecular weight gas at a low pressure. In terms of microshell manufacture, the choice of blowing gas relative to the application of the microshells is an important consideration. Gases such as  $\text{CO}_2$  and  $\text{SO}_2$  are normally used. Water has been referred to as steam. Metal vapor has been referred to. What is most economically reasonable depends upon technical and cost trade-offs as appropriate to the overall manufacturing process for microshell production and the specific application for such microshells.

Where suitable shells are not available for performing in-permeation and out-permeation, a method of shell manufacture is also disclosed which produces glass shells that are easily evacuated with the methods of this invention in order to achieve low internal pressures. A long vertical furnace utilizes steam as its furnace atmosphere, wherein water or steam is contained within glass particles that acts as a blowing agent to form the shells under furnace conditions. The resulting shells contain steam with trace amounts of air in its accompanying constituents. The shells are then in-permeated with hydrogen in order to react the trace gases and are subsequently raised to an elevated temperature and out-permeated to remove steam from the evacuated shells.

25 A consideration in insulation applications is the significance of radiative heat transfer. A low emissivity coating on microspheres can decrease radiative heat transfer. However, there are applications for which radiative heat transfer is of minor consequence, even for high emissivity. Thus the use of a reflective layer (low emissivity) is a design parameter and for some insulation applications is not of any real use, and not worth the expense.

30 The work by the authors on heat transfer studies has resulted in a thermal model that we have used to predict insulation layer performance, and also essentially confirm much of Torobin's reported results. As a result of these efforts, it is clear that much improvement in insulation performance can be achieved by using in the insulation layer small diameter (50 to 100 microns) high aspect ratio (shell outside diameter divided by average shell wall thickness) glass or polymer shells that are evacuated, or at least contain a low thermal conductivity gas.

At one extreme, insulation layers based upon evacuation high aspect ratio shells, when coated with a low emissivity, reflective layer, and evacuated space between the shells, the R-value/inch can approach that of super-insulation. For a reflectivity of 0.9, with all space evacuated, an R-value/inch of near 3000 is predicted for a microsphere diameter of 100 microns with a shell aspect ratio of 100 and negligible contact

conductance between the shells. Similarly, if the reflectivity drops to 0.0, i.e., a perfect absorber/emitter, then the predicted R-value/inch drops to about 300. For those insulation applications for which all the space within the insulation layer is evacuated, the role of layer reflectivity is especially important.

Clearly there is strong motivation for evacuated high aspect ratio shells that have low thermal conductivity wall material. Polymer shells have the advantage of lower thermal conductivity compared to glass. However, other physical properties of polymer shells restrict the use of such shells to more narrow temperature limits when compared to glass shells. For a much broader range of thermal insulation applications, glass microspheres are the preferred material and shape of interest.

One application of microshells employs such shells in a roof coating to enhance the insulation and improve the solar reflectivity characteristics of the coating. Preferably, the microshells are made of lower thermal conductivity glass and are evacuated. These microshells could be manufactured as evacuated, or could be evacuated after manufacture. Such an evacuation method is detailed.

For the case where microspheres must be evacuated, gaseous constituents which are trapped within the shells as a result of shell manufacture are reacted with hydrogen to form a gaseous mixture which can be removed through a procedure of out-permeation. Preferably, where oxygen is present within the glass shell, hydrogen is permeated through the walls of the shell to form a reactive gaseous mixture at elevated temperature. In this case, the hydrogen within the shell will react with oxygen to form steam. Other gases, for example carbon dioxide would react with the hydrogen to form carbon monoxide and steam. Further reactant gases within the shell will also react with the hydrogen, or else with the products of other hydrogen reactions. After completion of the reactions, the remaining hydrogen and other formed gases will be removed by out-permeation. During this out-permeation process, a partial vacuum is formed around the spheres to remove the gases.

For heat transfer applications for which radiative heat transfer is significant a highly reflective microshell coating is preferably formed on the shell to reduce the radiant heat transfer. Preferably, the reflective coating is a metal layer formed on the exterior of the shell. Alternatively, the reflective coating may be formed on the inner surface of the shell, preferably as a by-product of the product gases formed by the reactions within the microsphere.

Further additional advantages are provided by the present invention when utilizing microspheres constructed according to the teachings of this invention. Further thermal insulation value and utility is obtained when a plurality of such microspheres are assembled or nested together, particularly when forming a coating, since the highly spherical and hard shells resist flexing and maintain a point contact conduction relative to one another which reduces conduction therebetween. Such point contact significantly reduces interconnecting surface areas which greatly decreases conduction therebetween as well as conduction through a surface or a material formed from such spheres.

Objects, features and advantages of this invention are to provide a microsphere and method of making it which greatly increases thermal insulation value of a material constructed with such microspheres by reducing conduction, radiation, and convection therethrough.

Further objects, features and advantages of the invention will become apparent from a consideration of the following description and the appended claims when taken in connection with the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross-sectional schematic diagram of the microspheres, or shells, of this invention for forming thermally insulating materials;

FIG. 2 is a schematic diagram depicting a method of evacuating microspheres to form the thermally insulating microspheres of this invention;

FIG. 3 is a fragmentary cross-sectional view of a tile having an insulating coating constructed with the microspheres of this invention; and

FIG. 4 is a schematic diagram depicting a method of manufacturing glass microspheres having properties which facilitate easy evacuation by the techniques depicted in FIG. 2 to achieve low internal pressures.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

Referring in more detail to the drawings, FIG. 1 illustrates a small insulating microsphere 10 formed from a glass or polymer shell 12 having an evacuated interior 14 such that the microsphere provides reduced heat conduction and is optimal for constructing insulating materials and coatings. A highly infrared (IR) reflective coating 16 may be provided preferably on the exterior of shell 12 to reduce radiant heat transfer. Furthermore, a protective-low thermal conductivity transparent coating 18 may be provided over reflective layer 16 to protect the reflective coating from degradative processes.

Preferably, the reflective coating 16 is formed from a layer of metal which is deposited on the shell 12 to provide a highly reflective surface in the infra-red region. In the preferred version, the metal coating is formed on the outer surface of shell 12. Alternatively, reaction products resulting from the reaction of residual gases within the microsphere which are used in constructing the shell can be condensed out on the interior surface of the shell 12 to provide such an interior coating. In either case, the shell is preferably coated with a thin reflective coating generally of a metal such as Al, Zn, Ag, Cu, Au, Ni, or Sn with thicknesses in the range of 30 to 50nm and with emissivity of less than or equal to 0.04 in the IR (infra-red) range of radiation. Furthermore, such a reflective coating can be provided on both the interior and exterior of shell 12 in order to further enhance reflection, particularly in the infra-red region, which further enhances the insulation properties of microspheres as well as materials and coatings formed from such microspheres.

Preferably the glass or polymeric shells 12 are formed with a high AR (aspect ratio) in order to optimize thermal resistance. High AR refers to the ratio of the diameter of the shell to the shells wall thickness. The higher the AR the lower the shell wall conduction. An AR over 100 is desired. However, some applications will require insulation which bears high loads which will necessitate use of smaller AR's at the expense of thermal resistance.

When constructing microsphere 10, a substantially evacuated shell 12 is required to enhance the conduction properties of the microsphere. In order to achieve the desired evacuated microsphere, a method for evacuating such shells is described below. This process utilizes the permeation of gases through the walls of the shell at sufficiently high temperature to change and remove the residual gases within the shell which are formed during its manufacture. The types of residual gases remaining in the shells after manufacture are dependent on the specifics of each manufacturing process. For example, commercially available shells, not manufactured with subsequent shell evacuation as an anticipated step, often contain CO<sub>2</sub> and CO, or SO<sub>2</sub>



and O<sub>2</sub>. Certainly other blowing gases are alternatives, such as H<sub>2</sub>O, O<sub>2</sub>, other.

### Construction of Shells

5 In order to obtain viable evacuated shells 12 for constructing microspheres 10 of this invention, either a method is used to directly produce evacuated glass or polymeric shells or selected commercially available shells are evacuated using the methods of this invention in order to produce the evacuated shells required to construct the microspheres 10.

10 Blowing agents that lead to gases that can be more easily removed by the methods of this patent are first introduced into a glass mixture to obtain a homogenous mix for constructing such microspheres. The solid mixture of glass and blowing agents is then processed with existing, routine methods, e.g., the solid mixture can be subsequently crushed and the resulting frit particles introduced into a heated region where the particles are blown into shells. By choosing the blowing agents such that they are either low vapor pressure solids at room temperatures as exemplified by selected patents by Torobin including U.S. Patent No. 4,303,732, or by utilizing such blowing agents which can later be removed from the shells with an evacuation  
15 procedure, glass shells can be subsequently evacuated.

Where commercially available shells which are suitable for evacuation by the methods of this invention are not available, the following method is preferably used to directly produce suitable evacuated glass shells. First, raw materials for forming a desired glass composition are mixed. Secondly, the mixture of raw materials is reacted at low temperature to form a final composition of material. Then, the composition  
20 is partially dried, crushed, and size-separated into frit. Subsequently, a vertical furnace is used to form and blow glass shells at high temperature according to the below-mentioned procedure. The resulting completed shells are then separated from shell residue, and the shells are evacuated using the methods of this invention which removes water vapor from the shell interior. In this procedure, steam is utilized as the blowing agent during formation of the shells. The steam within the column results from the water which is retained in the injected glass frit, which has been only partially dried, and from steam separately injected into the column.  
25 Typically, the water is contained in the raw materials used in forming the composition. With this procedure, basic raw materials are combined to produce glass shells which are readily evacuated.

As shown in FIG. 5, a long vertical furnace 36 having an internal furnace atmosphere with steam 40 receives the glass frit material 38 and water or steamed contained in the frit which acts as a blowing agent  
30 to form the shells under the internal furnace atmosphere and thermal conditions. The furnace is non-hazardous and prevents the in-permeation of undesirable gaseous constituents as a direct result of the furnace atmosphere 40. The steam which forms within frit particles 38 under elevated temperature is relatively easily removed from the shells by high temperature evacuation through subsequent steps as described and shown in FIG. 2. The procedures for out-permeating the steam as described hereinafter are  
35 shown in FIG. 2 and are necessary to obtain evacuated microspheres having insulation properties with the highest resistance (or maximum R-value) to conductive heat transfer. The degree of evacuation that is attainable within the shells is a desirable design parameter when constructing insulating applications since loss of evacuation diminishes the insulating properties. Gaseous conduction therefore results which can only be decreased by further evacuation, or by the introduction of other gases having superior insulating properties  
40 therein. The typical characteristics of a glass shell wall, however, cannot be further tailored to improve

insulation. It is generally understood that internal pressure drops beyond a few Torr decrease the conductivity of the gases, and further pressure drops further decrease the conductivity. However, the shell conductivity of glass does not decrease in nearly the same magnitude in response to pressure drops, even when pressure has been decreased to a pressure of 30 mills-Torr.

5 When constructing frit particles 38 to produce shells 12 as shown in FIG. 6, the raw materials and constituents can be modified to provide alternatively produced glass shells 12 which further enhance effective evacuation. In particular, the in-permeation of hydrogen at elevated temperatures and a subsequent reaction of the hydrogen with certain gaseous constituents in a glass shell will allow removal of reaction product more easily. For example, oxygen inside a shell can be reacted with in-permeated hydrogen to form steam which  
10 is more easily and readily removed than the oxygen. Other approaches can be utilized to derive more readily and easily out-permeated gases using various other modified constituents within glass frit particles 38.

Further alternative variations can be provided wherein frit particles 38 contain metals which partially vaporize to blow the shell and which coat the inner surface of the shell. By adding an appropriate amount of metal, an appropriate thickness of an internal metal coating can be obtained which gives a high reflectivity (or  
15 a low emissivity), but which does not increase in thickness sufficiently to increase the shell thermal conductivity. Typically, an internal coating thickness of at least 10 nanometers is required. Furthermore, chemical vapor deposition is an alternative coating technique.

FIG. 2 shows the method for evacuating shells 12 of this invention when constructing the microspheres 10 depicted in FIG. 1. This method relies on the permeation through the walls of the shells by  
20 gases when subjected to sufficiently high temperatures.

The transfer of a gas across a shell wall is normally described as the permeation of the gas through the wall, and the rate of transfer is proportional to a pressure difference across the shell wall. A proportionally constant termed the permeability is a function of the wall material composition, the permeating gas composition, and temperature. This permeability is normally measured under steady-state conditions of a  
25 partial pressure driving force. It is, however, routinely used for describing the transient behavior of pressure within the shells when shell filling or emptying is done. In more fundamental terms, permeability is the product of the diffusivity and the solubility of the gas in the wall material. Qualitatively, permeability increases dramatically with an increase in temperature. Permeability is extensively discussed in "The Scientific Foundations for Vacuum Technology", S. Dushman, 2nd Edition, John Wiley and Sons, NY, 1962, pp.491-  
30 500, hereinafter incorporated by reference.

The rate of diffusion generally increases as the size (or molecular weight) of the permeating gases decreases; e.g., helium and hydrogen readily permeate shells, neon and argon permeate more slowly, oxygen and nitrogen permeate much more slowly, and gases such as CO<sub>2</sub> permeate negligibly even at maximum practical temperatures.

35 Based on the above, it is part of this invention to process the gases inside the shells in order to obtain product gases that can more readily permeate the shells.

In summary, the innovative method for evacuating glass micro shells of this invention uses the high permeability of glass to hydrogen and other gases and the reactivity of certain gases with such hydrogen to form other gases which can be more easily removed from the interior of the shells 12. To permeate hydrogen  
40 through glass shells 12 relatively rapidly, the temperature is elevated to a range of a few to several hundred

degrees Centigrade and total pressures of a few to several atmospheres are used which will allow the reaction of hydrogen with the other gaseous constituents within the manufactured shell. In practice, hydrogen which permeates into the shell comes from a mixture with non-permeable inert gas, such as nitrogen, which is provided on the exterior of the shells 12. Once the shells have been filled with hydrogen through permeation from an external gas mixture, the shells are maintained at a temperature which permits thermodynamically favored reactions to occur within the shells interior 14. For example, oxygen will combine with the hydrogen to form steam. Likewise, carbon dioxide when combined with hydrogen will form carbon monoxide and steam. Other reacting gases within the shell will also react with the hydrogen, or with the products of other hydrogen reactions. The temperature sometimes required will depend upon the original constituents present within the shells, which will depend on the manufacturing process used to construct the shells. The shell gaseous contents which result depend upon the methodology used in the shell manufacture and the starting glass-forming reactants.

Once the reactions have completed, the resulting hydrogen and other gases are removed by out-permeation into a partial vacuum relative to the gases to be removed. The amount of vacuum needed to achieve this result depends upon the time allowed for the out-permeation, the product gases which are formed by the reactions, the glass composition, and the temperature of the out-permeation.

As depicted in FIG. 2, a supply of hydrogen 20 and a supply of nitrogen 22 are mixed and fed into a permeation/reaction chamber 24. Spheres 12 having trapped gases therein 14 are fed into the permeation and reaction chamber 24 where they are exposed to a nitrogen and hydrogen mixture of gases while maintained at elevated temperature and elevated pressure. Preferably, the elevated temperatures reach at least a nominal 350°C and the pressure is at least a few atmospheres. In the preferred variation, the following reactions occur within the chamber:



after feeding these spheres through the permeation/reaction chamber 24, the spheres are received in an out-permeation chamber 26 where staged out-permeation occurs at elevated temperatures (nominal 350°C), and at a partial vacuum. The time and temperature for this out-permeation depends upon the glass and gas composition within each sphere 12. Subsequent to appropriate out-permeation of the gases in the chamber, shells are passed and directed onto conveyor 28 for delivery to packaging. Such shells are delivered with gases at reduced pressure and lower thermal conductivity. For example, construction of spheres according to FIG. 2 provide for spheres retained in permeation reaction chamber 24 for 3 or more hours at 350°C temperature and in the range of 3-10 atmospheres pressure. Subsequently, the cylinders are delivered to an out-permeation chamber 26 for 12 or more hours at 350°C temperature and in the range of 1-10 milliTorr pressure.

#### Construction of Insulation Coatings

FIG. 3 depicts a wall tile 30 having an insulation coating 32 retained on the tile which contains insulating microspheres 34 of this invention. Spheres 34 are constructed of hollow glass shells 12 having a metal coating 16. Such microspheres 34 are evacuated utilizing the methods of this invention to reduce conduction through the spheres. Alternatively, such a shell can be constructed of a plastic material.

Insulation coating 32 contains an admixture of binders, pigments, extenders, protective additives, in addition to the microspheres 34, which are joined and bonded together to form the insulation coating. The binders bond the coating to the tile 30 and solidify and enforce the coating which retains the microspheres therein.

- 5 Furthermore, such a coating can be used with or without the metal coating provided on each shell 12, depending upon the details of the specific application and requirements for the coating in use. Such coatings may also be used for roofs, for exterior paint and interior paint, and other uses. These evacuated shells provide a crucial component in formulating a coating which allows attainment of appreciably decreased thermal conductivity, and helps develop and retain a high reflectivity to solar and other infra-red radiation. A  
10 combination of long-term high IR reflectivity and low thermal conductivity decreases the energy loading, resulting from absorption and transference of heat, into a coated enclosure. For example, such a coating could be utilized within an infra-red oven to retain heat more efficiently therein and enhancing the cooking operation of process.

- When formulating elastomeric roof coatings and exterior paints, it is desirable to utilize the evacuated  
15 spheres 12 in combination with other high quality constituents to obtain a coating which is especially reflective of solar radiation, which has a low thermal conductivity, and appreciable reduces cooling and air conditioning power cost due to the increased solar reflectivity and lower thermal conductivity. These coatings are preferably elastomeric to obtain excellent long-term adhesion to a variety of surfaces. An example of a preferred formulation of an elastomeric roof coating, based upon highest quality constituents and glass shells  
20 is as follows:

<u>Item No.</u>	<u>Material</u>	<u>Mass lbs.</u>	<u>Volume Gal.</u>
1	Water	84.50	10.14
25 2	Troysan 186	2.00	0.24
3	KTPP	1.25	0.05
4	Tamol 850	8.00	0.81
5	TiO <sub>2</sub> ,Kronos 2102	152.00	4.56
6	ZnO ZOCO 103	31.00	0.66
30 7	SIFT IN THE NEXT ITEM		
8	Natrosol 250 HBR	1.00	0.09
9	PA-328	5.25	0.75
10	Propylene Glycol	34.56	4.00
11	GRIND UNTIL SMOOTH		
35 12	Rhoplex EC 2540	423.50	48.34
13	Texanol	7.00	0.88
14	Skane M8	1.60	0.19
15	PA-328	5.76	0.82
16	Glass/polymer Shells	50.00	30.12

17	Acrysol RM-825	$\frac{0.68}{808.10 \text{ lbs.}}$	$\frac{0.08}{101.74 \text{ gal.}}$
			density 7.94 lbs/gal

Preferably, the diameter of shells 12 utilized in the formulation of microspheres 34 when constructing the above roof coating or insulation coating 32 is dependent highly upon the details of the formulation, and especially the nominal required thickness for the dry coating film. For most coatings, the microsphere 32 will have a diameter nominally of 20-100 microns. For an insulation coating 32 which is utilized on a roof, the diameter range of the shells could be larger. The nominal wall thickness range of the shells would be from less than 1 to several microns, depending upon the method of applying the coating to the substrate and thus the corresponding strength demands for the shells.

10 The shells 10 utilized in constructing the coating 32 can be purchased from several manufacturers including K-25™ as manufactured by Minnesota Mining and Manufacturing Company of 3M Company, 3M Center, Saint Paul, Minnesota. The evacuation of these commercially available shells can be accomplished as described infra utilizing the techniques of this invention. Furthermore, other various known techniques for evacuating shells may be utilized.

15 A further example of a thermal insulating coating of this invention is apparent where water is used as a binding agent with evacuated microspheres to provide a packing insulating material for application to an animal's injured leg, for example for application on a horse. Such a packing would provide heat retention to the injury which functions as a thermal insulating bandage or heat pack.

It is to be understood that the invention is not limited to the exact construction illustrated and described above, but that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the following claims.

**CLAIM**

1. A thermal insulating material for reducing heat transfer between a first and second location comprising:  
a plurality of substantially evacuated hollow microspheres clustered proximate one another  
5 to provide an insulating layer.
2. The thermal insulating material of claim 1 further comprising a binder admixed with said microspheres to form a concretion therebetween.
- 10 3. The thermal insulating material of Claim 2 wherein said microspheres are formed from a hollow glass shell having a reflective film provided on said shell wherein said binder is an elastomeric coating for reflecting solar radiation.
4. The thermal insulating material of Claim 3 further comprising a UV absorptive pigment  
15 provided in said elastomeric binder.
5. The thermal insulating material of Claim 3 wherein said elastomeric binder is latex.
6. The thermal insulating material of Claim 5 further comprising an acrylic binder in combination  
20 with said latex vehicle for providing insulating roof coating.
7. The thermal insulating material of Claim 5 further comprising an acrylic binder in combination with said latex vehicle for providing an insulating reflective paint.
- 25 8. The thermal insulating material of claim 1 wherein said microspheres are formed from a hollow glass shell.
9. The thermal insulating material of claim 1 wherein said microspheres are formed from a hollow polymeric shell.

30

10. The thermal insulating material of claim 8 further comprising a reflective film provided on said glass shell.

11. The thermal insulating material of claim 10 wherein said reflective film is a metallic coating  
5 selected from the group consisting of Al, Ag, Cu, Au, Ni or Sn, said coating providing infra-red reflective characteristics.

12. The thermal insulating material of claim 10 wherein said film is provided on an outer surface of said shell.

10

13. The thermal insulating material of claim 10 wherein said film is provided on an inner surface of said shell.

14. The thermal insulating material of claim 12 further comprising a low conductivity coating  
15 provided over said film, said coating operable to protect said film from degradation.

15. The thermal insulating material of claim 11 wherein said metallic coating forms a thin layer less than  $0.5\mu\text{m}$  in order to minimize heat transfer through the coating, said coating providing an emissivity in the infra-red range of  $\leq 0.04$ .

20

16. The thermal insulating material of claim 9 further comprising a metallic coating provided on an exterior of said shell, said coating operable as a barrier to permeation by ambient gases and further functioning as a reflective layer.

25 17. The thermal insulating material of claim 9 further comprising a reflective coating provided on said shell and a low conductivity coating further provided on the exterior of said shell, wherein said low conductivity coating provides a barrier to permeation by ambient gases.

18. A method for producing hollow microspheres comprising:  
30 providing an add mixture of glass particles and blowing agent;

introducing the blowing agent into the glass frit particles;

heating the glass frit particles and blowing agent in a furnace at temperatures such that the viscosity of the glass is sufficiently low that a liquid glass droplet is formed and the blowing agent vaporizes to form blowing gasses, upon which the liquid glass droplet is blown into a glass bubble;

5 cooling the glass bubble by removing it from the furnace which rapidly solidifies to form a hollow glass shell.

19. The method of claim 18 wherein the blowing agent produces steam as the blowing gasses.

10 20. The method of claim 18 wherein the blowing agent comprises small metallic particles of low vapor pressure solids which vaporize to produce the blowing gasses, wherein the remaining portions of metal coat the inside of the resulting glass bubble.

21. A method of claim 18 wherein the blowing agent is a silica sol gel.

15

22. A method for producing hollow microspheres comprising:  
coating small metal particles with glass;

heating the glass coated metal particles such that the glass flows to encapsulate the metal particles and the metal particles subsequently vaporize to generate blowing gases to form a glass bubble;

20 and

cooling and solidifying the glass bubble to form a glass shell with a vacuum inside the shell and an IR reflective metal coating formed on the interior of the walls of the glass shell.

23. The method of Claim 22 wherein chemical vapor deposition is utilized to coat said small  
25 metal particles.

24. The method of Claim 22 wherein RF sputter deposition is utilized to coat said small metal particles.

30



25. A method for evacuating hollow microspheres comprising:

providing microspheres having readily-reacting trapped gases therein;

in-permeating said microspheres with reaction gases wherein the trapped gases and the reaction gases react at elevated temperatures and pressures to produce product gases readily permeable

5 to the microspheres; and

out-permeating said product gases at elevated temperatures and partial-produced pressure to remove such reaction gases from the microspheres.

FIG 1

1/2

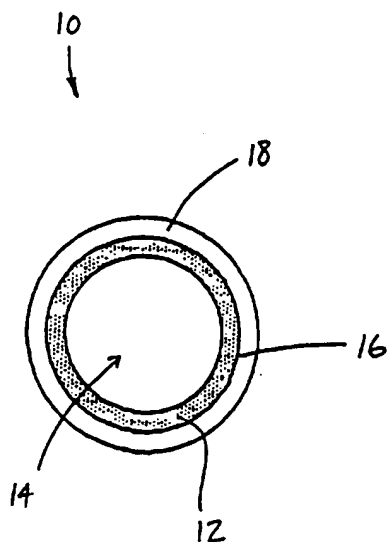


FIG 2

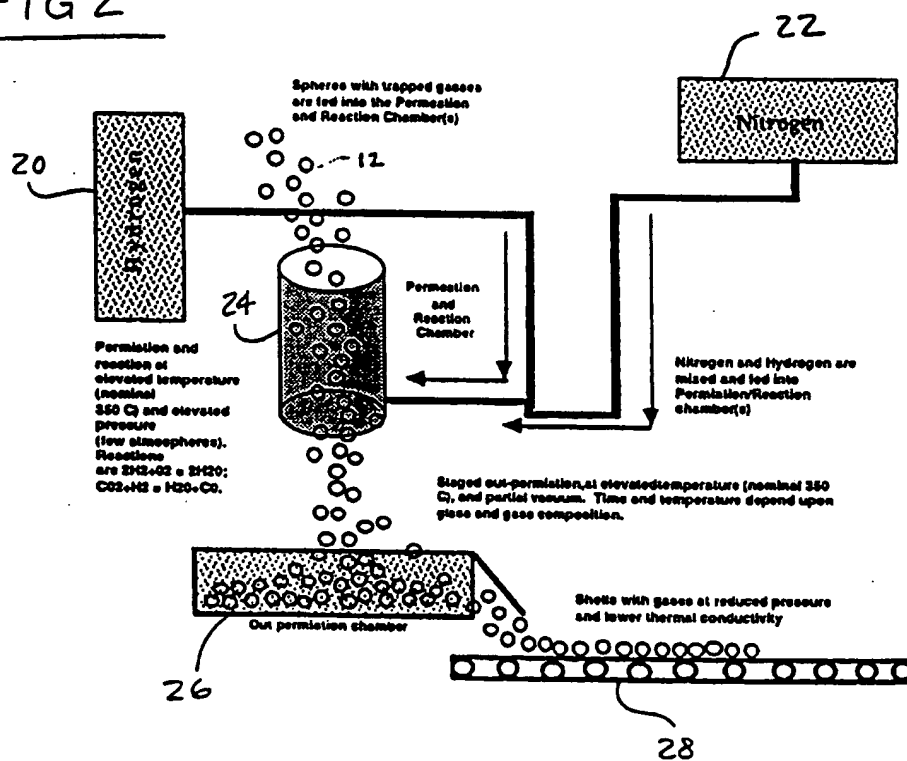
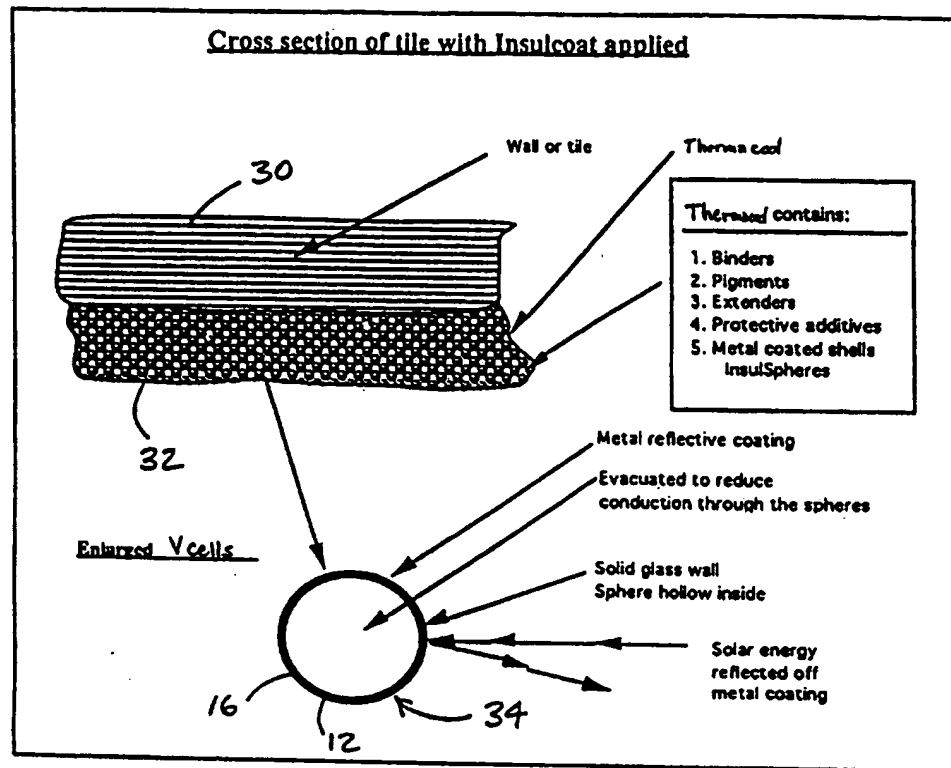
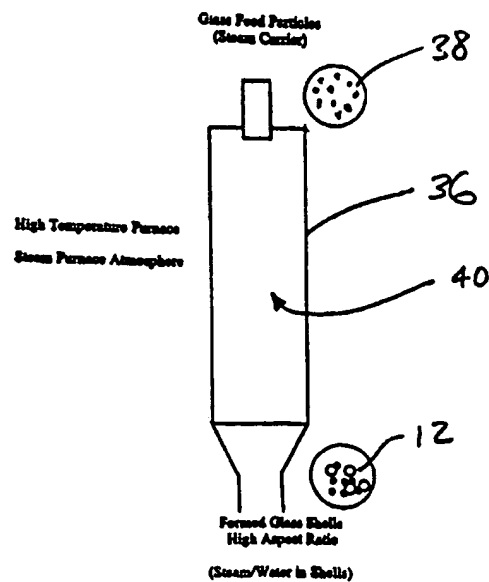


FIG 3

2/2

FIG 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/11340

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/402, 402.2, 402.21, 403, 404, 406, 406, 407; 427/585, 213.31, 214, 217, 220, 222; 65/21.4, 60.1, 60.4, 60.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: microspheres, insulation, low emissivity, reflective

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US, A, 3,607,169 (COXE) 21 September 1971, see column 1, lines 52-75; column 2, line 41 to column 3, line 15.	1, 8-11, 13, 18-20, 22 ----- 2-3
Y	US, A, 4,303,732 (TOROBIN) 01 December 1981, see column 5, line 25-63; column 6, line 64 to column 7, line 6; column 7, line 24 to column 8, line 56; columns 18-19.	1-2, 5-8, 10-11, 13, 18-20, 22
Y	US, A, 4,303,736 (TOROBIN) 01 December 1981, see column 12, line 47 to column 16, line 35; column 22, line 50 to column 25, line 50.	1-2, 5-7, 9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention
* A document defining the general state of the art which is not considered to be of particular relevance	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E earlier document published on or after the international filing date	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* A	document member of the same patent family
* O document referring to an oral disclosure, use, exhibition or other means		
* P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 NOVEMBER 1995

Date of mailing of the international search report

07 DEC 1995

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

VIVIAN CHEN

Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/11340

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,303,061 (TOROBIN) 01 December 1981, see column 7, line 25 to column 8, line 55; columns 18-19; column 27, line 42 to column 31, line 68.	1-2, 5-8, 10-11, 13, 18-20, 22
Y	US, A, 4,582,756 (NIINUMA ET AL) 15 April 1986, see column 2, line 63 to column 3, line 64.	1-2, 9, 14, 17
Y	US, A, 3,769,770 (DE CHAMPS ET AL) 06 November 1973, see column 1, line 64 to column 2, line 39; column 2, line 63 to column 4, line 2.	3, 8, 10-12, 14, 16-17, 23-24
A	US, A, 4,039,297 (TAKENAKA) 02 August 1977, see column 3, lines 23-26.	3, 8-12, 23

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US95/11340

**A. CLASSIFICATION OF SUBJECT MATTER:**

IPC (6):

B32B 5/16, 9/00, 15/02, 17/02, 17/04, 27/02, 27/04; B01J 13/02, 13/04, 13/20, 13/22; C23C 14/00, 14/58, 20/02, 20/04; C03B 19/10, 19/12, 19/14, 37/00; C03C 17/06, 17/34, 17/36, 25/02, 25/04

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

428/402, 402.2, 402.21, 403, 404, 406, 406, 407; 427/585, 213.31, 214, 217, 220, 222; 65/21.4, 60.1, 60.4, 60.5